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(54) Title: A HERBICIDAL COMPOSITION COMPRISING GLYPHOSATE AND AN N-ACYLSARCOSINATE

(57) Abstract

This invention concerns herbicidal compositions comprising N-phosphonomethyl glycine and/or one or more herbicidally active derivatives thereof and an N-acyl sarcosinate surfactant. Such compositions exhibit greatly reduced eye irritation to the user while maintaining their herbicidal efficacy.

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A HERBICIDAL COMPOSITION COMPRISING GLYPHOSATE AND AN N-ACYLSARCOSINATE

Field of the Invention

The present invention relates to herbicidal glyphosate compositions, exhibiting greatly reduced eye irritancy, when compared to commercial glyphosate compositions.

Background

Glyphosate or N-phosphonomethyl glycine is well-known as a broad-spectrum herbicide. It acts as a postemergent herbicide which is translocated within plants. Typical commercial formulations contain about 41% of the isopropylamine salt of glyphosate and about 5%-20% by weight of a tallow amine ethoxylated surfactant.

Surfactants are typically incorporated into the formulation to improve the efficacy of glyphosate. These surfactants are termed activating surfactants. The term surfactant may include a number of compounds. For example, with ethoxylated surfactants the degree of ethoxylation can be and typically is a statistical mixture.

Numerous studies have been made on the effect of additives on the herbicidal activity of glyphosate. For example Wyrill and Burnside , Weed Science, Vol 25 (1977), 275-287, examined solutions containing different classes of surfactant, including 2 and 15 oxyethylene units. Some classes of surfactant were more effective than others in enhancing the herbicidal activity of glyphosate. However, Wyrill and Burnside concluded that a surfactant is a critical component of any glyphosate spray mixture.

Ethoxylated alkyl amine surfactants present in glyphosate formulations have been observed to greatly increase the corrosivity or irritancy of the composition to the eyes. The level of irritancy is such that commercially formulated glyphosate solutions containing ethoxylated alkylamine surfactants must be labelled as an irritant.

WO 97/03560 of Hampshire Chemical Corporation discloses herbicidal fluazifop-butyl (or fluazifop-P-butyl) compositions containing a C_8 to C_{22} sarcosinate or sarcosinate salt, such as sodium cocoyl sarcosinate, sodium lauroyl sarcosinate or combinations thereof. The sarcosinate may be used at concentrations of 0.1 to 3.0% v/v in the formulation. WO 97/03560 does mention lower irritancy and lower toxicity which may be attributed to the use of an aqueous solvent instead of an organic solvent which had been previously necessary to provide a solution of fluazifop-P-butyl. The use of an aqueous solvent in place of an organic solvent would in reality provide lower irritancy. This is confirmed by the fact that the inventor does not provide any evidence of lower irritancy. WO 97/03560 contains no teaching about herbicidal glyphosate compositions. It could not be foreseen whether the use of a sarcosinate or sarcosinate salt in glyphosate compositions would have an adverse effect on the efficacy of glyphosate as the herbicide fluazifop-butyl is substantially different in its chemical structure and its mode of herbicidal action from glyphosate. Sarcosinates are themselves classified as eye irritants when in a 30% w/w aqueous solution.

Object of the Invention

It is an object of the present invention to provide a glyphosate composition which exhibits reduced irritation in particular to the eye without loss of efficacy of the herbicidal composition.

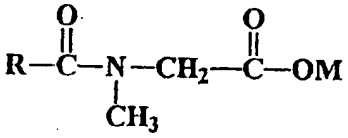
It is a further object of the present invention to significantly reduce the cost of preparation of glyphosate formulations. It is a further object of the present invention to significantly reduce the cost of such formulations in an environmentally friendly manner by the addition of lower amounts of surfactants without loss of efficacy. It is also desirable to produce a composition which does not display phytotoxicity.

Summary of the Invention

The present invention provides a herbicidal composition comprising :

(a) a herbicidally effective amount of N-phosphonomethyl glycine and/or a herbicidally active derivative of N-phosphonomethyl glycine or mixtures of N-phosphomethyl glycine and a herbicidally active derivative of N-phosphonomethyl glycine or mixtures of derivatives of N-phosphonomethyl glycine; and

(b) an effective amount of at least one surfactant of the formula



wherein R represents an optionally substituted, saturated or unsaturated hydrocarbyl C_1-C_{40} group for example an alkyl or alkenyl group having up to 40 carbon atoms, and M is H or a positively charged counter ion.

This composition with the particular combination of glyphosate and an N-acyl sarcosinate surfactant demonstrates reduced eye irritancy as compared to conventional glyphosate compositions. Surprisingly the herbicidal compositions of the present invention, utilising N-acyl sarcosinates at a much-reduced level as a percentage weight of the total formulation compared to conventional surfactants, exhibit no loss of efficacy. In glyphosate solutions, conventional surfactants are used at 6 to 17% by weight of the total formulation.

The sarcosinate surfactant used in the composition of the present invention may be used at concentrations as low as 0.1% to 2% of the total formulation. The eye irritancy of such compositions has been found to be greatly reduced, which is surprising as formulations traditionally carry irritancy labels and the solvent has not been changed. The compositions of the present invention do not need to be labelled as irritants.

R preferably has 8 to 22 carbon atoms, more preferably 10 to 18 carbon atoms. R may be straight chain or branched and may be substituted with halogen, preferably Cl or F, or OH or an alkoxy group, a carboxylic acid derivative or an alcohol derivative. The alkoxy group preferably contains 1 to 8 carbon atoms, more particularly 1 to 4 carbon atoms.

M is desirably selected from the group consisting of alkalis, alkali metals and alkaline earth metals for example, sodium or potassium, or ammonium, alkylamine or aminoalcohol. Preferably the alkylamine comprises 8 to 22 carbon atoms, more preferably 10 to 18. Suitably the aminoalcohol comprises 1 to 22, preferably 2 to 18 carbon atoms. Suitably the surfactant is present from about 0.1% to 40% wt/wt of the composition. However concentrations from about 0.1% to 20%, preferably 0.1% to 5%, more preferably 0.1% to 2% by weight of the composition may be used. The composition may optionally comprise at least one additional surfactant. Additional surfactants which may be used include those used in conventional glyphosate compositions.

The invention also relates to a method of controlling weeds, said method comprising applying to the weeds and the locus in which they grow a herbicidally effective amount of a herbicidal composition described above. Another feature of the invention is a method of controlling weeds growing among a crop of glyphosate-resistant genetically engineered plants, comprising applying to the weeds and the crop a herbicidal composition described above. It is known that plants such as sugar beet which have been genetically engineered to be glyphosate-resistant are available. The herbicidal composition may be diluted with water prior to application.

Surprisingly the N-acyl sarcosinate surfactants themselves when sprayed on vegetation exhibit no phytotoxicity to the vegetation and in some instances appear to enhance growth. This is a very useful attribute

of any surfactant particularly when a composition containing the surfactant is applied to a herbicide-resistant genetically engineered crop. For example, the composition may be diluted to a concentration that is typically sprayed from 100 - 450 g/litre acid equivalent solutions.

Detailed Description of the Invention

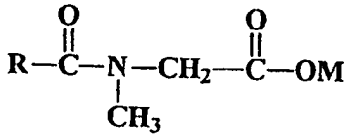
Glyphosate, and its herbicidally active derivatives, particularly its salts, or mixtures thereof which act as the herbicidally active ingredients of the composition of the present invention can be prepared by a variety of oxidations of phosphonoiminodiacetic acid, (PMIDA), that are well known in the art. For example, US patent number 3,954,848 discloses the production of glyphosate by the acid catalysed oxidation of PMIDA. Specifically PMIDA is mixed with water and an acid and the mixture is heated to elevated temperatures. An oxidising agent such as hydrogen peroxide is added to convert the PMIDA to glyphosate, which is subsequently isolated by precipitation. US patent 3,969,398 discloses the oxidation of PMIDA to glyphosate employing molecular oxygen in the form of air, oxygen or oxygen diluted with helium, argon, nitrogen or other inert gasses. Activated carbon is employed as a catalyst. US patent 4,147,719 discloses production of certain mono- and di-salts of glyphosate in a single aqueous reaction system by oxidising a salt of PMIDA with a molecular oxygen-containing gas in the presence of platinum supported on an activated carbon substrate. The oxidation reaction is carried out at elevated pressures ranging from 1.5 to 5 kg/cm^2. US patent 4,898,972 discloses the production of glyphosate by the oxidation of PMIDA using cobalt or manganese salts in the presence of bromide. US patent 4,002,672 discloses the production of glyphosate by the acid catalysis of PMIDA. PMIDA is contacted with a strong acid having a pKa of less than 2.2, at an elevated temperature so as to cause the decomposition or hydrolysis of PMIDA to N-phosphonomethyl glycine. US patent 4,696,722 discloses how the activity of a carbon catalyst can be enhanced by first removing the oxides of carbon from the surface. Any of these methods can be used to produce the glyphosate for use in compositions of the present invention.

Neutralisation of the glyphosate can be effectuated by any suitable base to form a herbicidally active derivative of glyphosate. These

suitable bases include alkali metal, alkaline earth metal or ammonium hydroxides and alkyl amines. Preferred glyphosate salts upon neutralisation include the mono(trimethylamine), mono(diethylenetriamine), mono n-propylamine, mono isopropylamine, mono sodium salt or mono potassium salt of N-phosphonomethyl glycine. Those skilled in the art will appreciate that the corresponding di and tri salts of N-phosphonomethyl glycine can be prepared by an appropriate increase to the amount of base added on neutralisation.

Certain surfactants are known to act in glyphosate formulations as activators that increase the biological activity of glyphosate. Ethoxylated amines are considered by those skilled in the art to be the most effective surfactants which may be employed in glyphosate solutions (c.f. Wyril and Burnside referenced above). Wyril and Burnside concluded in the reference given that the effectiveness of amine-containing surfactants increased with corresponding increases in the hydrophile-lypophile balance (HLB) and the degree of ethoxylation of the surfactant. As a result of these findings commercially formulated glyphosate compositions contain alkyl amine ethoxylates, and in particular, tallow amine ethoxylates. In these commercial formulations the amount of surfactant added is from about 0.1% to 20%, (wt/wt), of the formulation with the actual amount depending on the particular surfactant employed.

The activating surfactants for use in the present invention are N-acyl sarcosinates having the following general formula:



wherein R preferably represents an alkyl or alkenyl group having from 1 to 40 carbon atoms, preferably 8 to 22 carbon atoms and more preferably 10 to 18 carbon atoms, and M is H or a positively charged ion. M functions as a counterion to balance the negative charge on the other part of the molecule.

The N-acyl sarcosinate is suitably oleoyl sarcosinate, cocyl sarcosinate or lauroyl, stearoyl or other N-acyl sarcosinates having long unsaturated (C_8-C_{22}) carbon chain.

To prepare the composition of the present invention, the surfactant (N-acyl sarcosinate) may be incorporated into the formulation prior to neutralisation of the glyphosate acid with isopropyl amine or any suitable base. Alternatively, the N-acyl sarcosinate can be added to a glyphosate or glyphosate salt solution. Subsequent adjustment of the pH with a suitable base such as isopropyl amine can be conducted. Alternatively, the surfactant and a suitable base such as isopropylamine can be admixed prior to addition to the glyphosate solution.

Concentrated liquid compositions can be prepared by simple mixing operations. However it will also be obvious to those familiar with the art that solid powder or granular formulations can also be prepared by simple mixing of glyphosate or an active derivative of glyphosate or mixtures of glyphosate and/or mixtures of active derivatives of glyphosate with a solid surfactant.

Apart from the aforementioned additives the compositions according to the present invention can contain other components, in particular one or more other surfactants, formulation agents, anti-foams, corrosion inhibitors, sequesterants, penetrating agents, antifreezes and adhesives.

By way of illustration, given without implied limitation, examples according to the invention, as well as examples of use of these solutions are given below.

Example 1:

To 77.70g of 62% mono-isopropyl amine salt of glyphosate was added 2.28g of Oleoyl sarcosinate (Hamposyl O (TM) available from Hampshire Chemical Corporation, Teeside, UK). 34.55g of water was charged under agitation. The solution was neutralized to a pH of 5.60 with isopropylamine. The solution was observed to be stable.

Example 2:

To 77.70g of 62% mono-isopropyl amine salt of glyphosate was added 2.1g of

Cocoyl sarcosinate (Hamposyl C (TM) available from Hampshire Chemical Corporation, Teeside, UK). 34.00g of water was charged under agitation and the solution was neutralised to a pH of 5.2 with isopropyl amine (98%). The solution was observed to be stable.

Example 3:

To 77.70g of 62% mono-isopropyl amine salt of glyphosate was added 2.3g of Cocoyl sarcosinate isopropyl amine salt under agitation. 34.00g of water was charged under agitation and the solution was found to be clear and stable.

Example 4:

To 77.70g of 62% mono-isopropyl amine salt of glyphosate was added 2.3g of Oleoyl sarcosinate isopropyl amine salt under agitation. 34.00g of water was charged under agitation and the solution was found to be clear and stable.

Example 5:

The solution from example 4 was diluted to 1% glyphosate acid equivalent solution. This was done to get approximately the same concentrations as in commercially available glyphosate formulations (i.e. 0.1 kg of glyphosate acid was applied per acre) and sprayed on four 20X10 ft plots of mixed broad leaf weeds and grasses to evaluate the performance of the herbicide. A commercial formulation available from Monsanto Inc. under the trade mark Round Up and also containing glyphosate as an active herbicidal ingredient at a concentration of 360g per litre acid equivalent was similarly diluted to the same active concentration and sprayed on another 20X10 ft plot. A sample of oleoyl sarcosinate isopropylamine salt alone, (without the addition of glyphosate), but similarly diluted with water was also sprayed on a separate 20X10 ft plot at the same concentration as the solution of Example 4. Percentage chlorosis and % dry weight was estimated for each plot the results of which are listed in Table I. The percentage chlorosis was based on the observed yellowing of the weeds/grass of the plot. The solution from example 4 showed herbicidal activity comparable to the commercial

formulation used. The plot in which the surfactant alone was sprayed demonstrated no phyto-toxicity whatsoever and the vegetation in the plot continued to grow slightly better than that in the control plots which were untreated.

The percentage overall kill is given in Table II. The overall kill was judged visually by the browning or burn demonstrated by the grass/weeds of each plot.

TABLE I

	% CHLOROSIS after no. of days	
Formulation	5 days	10 days
Solution from example 4 diluted to 1% glyphosate acid equivalent	20	20
Round Up	15	15
Oleoyl sarcosinate isopropylamine (control)	0	0

TABLE II

	% Overall Kill (Visual: Burn/Browning)		
Formulation	8 Days	15 Days	21 Days
Solution from Example 4 diluted to 1% acid equivalent	12	30	65
Round Up	11	31	62
Oleoyl Sarcosinate Isopropylamine (Control)	0	0	0
Control Plot	0	0	0

Example 6:

A sample of the liquid composition described in example 4 was tested in New Zealand white rabbits to assess the irritancy potential of the test material. The method used followed that described in the OECD Guidelines for Testing of Chemicals No. 405, 'Acute eye irritation/corrosion' (adopted 24 February 1987) and method B5 of Commission Directive 92/69/EEC, (which constitutes Annex V of Council Directive 67/548/EEC). The results can be used as a basis for classification and labelling under Annex V1 of Council Directive 67/548/EEC relating to classification, packaging and labelling of dangerous substances.

The test results showed that a single instillation of the test material to the non-irrigated eyes of three rabbits produced minimal to moderate conjunctival irritation. All treated eyes appeared normal on observation 24 hours after instillation.

The test material produced a maximum score of 5.3 and was classified as a minimal irritant, (class 3 on a 1 to 8 scale), to the rabbit eye according to a modified Kay and Calandra classification system. As a result, the material did not meet the criteria for classification as an irritant according to EU classification regulations. The material does not therefore have to be labelled as an irritant. No symbol and risk phases are required on labels for the test material and no irritancy label.

(Comparative) Example 7

Eye Irritancy Test

Commercial glyphosate formulations containing alkyl amine ethoxylates, such as tallow amine ethoxylates, have been shown to be moderate irritants to the rabbit eye, as indicated by the label. A single application of a 50% aqueous dilution of a commercial formulation sold under the trade name Round - Up (360g/litre glyphosate acid equivalent) to the eye of a rabbit produced dulling of the normal luster of the cornea, irridial inflammation, petechial hemorrhage of the conjunctival membranes and severe conjunctival irritation. As a result it is assumed that the undiluted test material of

the commercial formulation is also at least a moderate irritant to the rabbit eye. Further tests using the undiluted material were not performed on rabbits as it was considered inhumane and unethical.

The 50% (w/v) aqueous dilution of the test material produced a maximum total score of 23.0 after 3 hours and was considered to be at a least moderate irritant, (Class 5 on a 1 to 8 scale) to the rabbit eye according to a modified Kay and Calandra classification system.

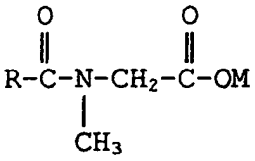
All testing of the experimental samples and commercial formulation was conducted in accordance with that described in OECD Guidelines for Testing of Chemicals (1987) No 405 "Acute Eye Irritation/Corrosion" referenced as method B5 in Commission Directive 84/449/EEC.

CLAIMS

1. A herbicidal composition comprising:

(a) a herbicidally effective amount of N-phosphonomethyl glycine and/or one or more herbicidally active derivatives thereof; and

(b) an effective amount of at least one surfactant of the formula



wherein R represents an optionally substituted saturated or unsaturated C_1 - C_{40} hydrocarbyl group and M is H or a positively charged counter ion.

2. A herbicidal composition according to claim 1, wherein R has 8 to 22 carbon atoms, preferably 10 to 18 carbon atoms, and/or M is selected from alkalis, alkali metals, such as sodium or potassium, alkaline earth metals, ammonium, alkylamines and aminoalcohols.

3. A herbicidal composition according to claim 1 or 2, wherein R is alkyl or alkenyl.

4. A herbicidal composition according to any of claims 1 to 3, wherein the surfactant is oleoyl, cocyl, lauroyl, stearoyl or other N-acyl sarcosinate having an unsaturated C_8 to C_{22} carbon chain.

4. A herbicidal composition according to any of claims 1 to 3, wherein the surfactant is oleoyl, cocyl, lauroyl, stearoyl or other N-acyl sarcosinate having an unsaturated C_8 to C_{22} carbon chain.

5. A herbicidal composition according to any of claims 1 to 4, wherein the surfactant is present from about 0.1% to about 40% wt/wt of the composition.

6. A herbicidal composition according to claim 5, wherein the surfactant is present from about 0.1% to 20% wt/wt of the composition.

7. A herbicidal composition according to claim 6, wherein the surfactant is present from about 0.1% to 5%, preferably from about 0.1% to 2% wt/wt of the composition.

8. A herbicidal composition according to any preceding claim, further comprising at least one additional surfactant, and optionally one or more of formulation agents, anti-foams, corrosion inhibitors, sequestrants, stabilizers, penetrating agents, anti-freezes and adhesives.

9. A method of controlling weeds, said method comprising applying to the weeds and/or the locus in which they grow a herbicidally effective amount of a composition according to any preceding claim.

10. A method of controlling weeds growing among a crop of glyphosate resistant genetically engineered plants, comprising applying to the weeds and the crop and/or the locus in which they grow a herbicidal composition according to any of claims 1 to 8.

INTERNATIONAL SEARCH REPORT

Int. tional Application No
PCT/IE 98/00086

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N57/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CROPU CRUDDEN J.J.: "N-acyl sarcosinates: effective, ecofriendly adjuvants for pesticide formulation." XP002092366 AN 96-86246 see abstract & "Abstr. Pap. Am. Chem. Soc., 211 Meet., AGRO 194" 1996 , AMERICAN CHEMICAL SOCIETY ---	1-10
X	WO 96 20593 A (HAMPSHIRE CHEMICAL CORP.) 11 July 1996 see page 2, line 13 - line 26 see page 5, line 20 - line 28 --- -/--	1-10

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
5 February 1999	18/02/1999

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Int ional Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category ³	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 03560 A (HAMPSHIRE CHEMICAL CORP.) 6 February 1997 cited in the application	

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte ional Application No
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